Effect of forced carbonation on the behavior of a magnesia-stabilized clay soil

A. R. Estabragh

Professor. Faculty of Soil and Water Engineering, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
ORCID: 0000-0003-4545-2310
Corresponding Author: A.R. Estabragh
Tel: +98 26 32241119
Fax: +98 26 32226181
Email: raeesi@ut.ac.ir

H. Khajepour

Postgraduate Student, Faculty of Soil and Water Engineering, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
Tel: +98 26 32241119
Fax: +98 26 32226181
Email: khajepour.hossein@ut.ac.ir

A.A. Javadi

Professor. Computational Geomechanics Group, Department of Engineering, University of Exeter, Devon, EX4 4QF, UK
Tel: +44 1392 723640
Fax: +44 1392 217965
Email: a.a.javadi@exeter.ac.uk

M. Amini

Postgraduate Student, Faculty of Soil and Water Engineering, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
Tel: +98 26 32241119
Fax: +98 26 32226181
Email: amini.mohadeseh@ut.ac.ir

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Abstract

Research on the method of forced carbonation on magnesium stabilized soil is limited. This paper presents an investigation into the behavior of a clay soil stabilized with MgO under forced carbonation and comparison with conventional chemical stabilization methods. The tests were conducted in two groups. In the first group the soil was mixed with 5, 10, 15 and 20% MgO or cement. Atterberg limits and compaction tests were conducted on these mixtures. Also, unconfined compressive strength (UCS) tests were performed on compacted samples from these mixtures at curing times of 7, 14 and 28 days. In the second group, samples prepared with different percents of MgO were subjected to CO_2 under pressures of 0.5, 1.0 and 1.5 bar for periods of 4, 8, 12 and 24 hours. The results showed that adding MgO increases the strength of the soil and, like other binders, the amount of increase in strength depends on the percent of MgO and curing time. It is also resulted that the effect of MgO is less than cement in increasing the strength. It was revealed that forced carbonation can facilitate the stabilization of MgO-stabilized soil in a few hours compared with usual process that takes several days. XRD and SEM results showed that the gained strength is resulted from the interaction between the soil and the agents.

Key words: Soil stabilization, Magnesia, Cement, Carbonation, Strength

Introduction

Soil stabilization is commonly conducted to improve the physical and mechanical behavior of soil. The stabilization technique depends on the type of soil and can be categorized to those that are applicable to noncohesive or cohesive soils. One of the stabilization methods that can improve the behavior of cohesive soils is using chemical stabilizers. In this method a small quantity of chemical additives is added to the soil and chemical reactions that occur between soil particles and chemical stabilizer result in improving the properties of the soil. Cement is one of the chemical stabilizers that is widely used for soil stabilization (Puppala et al., 2003, Chew et al., 2004 and Estabragh et al., 2016). Manufacturing 1 t of Portland cement requires about 5000 MJ energy and produces 0.95 t CO_2 during the calcination process of limestone (Higgins, 2007). Due to the economic, environmental and energy costs of cement, researchers have tried to introduce alternative agents with low carbon emission and low energy consumption during production. MgO (Magnesia) is one of the chemical stabilizers that has been recently introduced for stabilization of soils (Harrison, 2001 and Unluer and Al-Tabbaa, 2013). It is produced from $MgCO_3$ at temperature between 700-800^{0}C. A lower energy is needed for production of MgO in comparison with cement that is produced at 1450^0 C (Al-Tabbaa, 2013). MgO is also produced at temperatures of 1000-1400 and 1400-2000^0 C. Unluer and Al-Tabbaa, (2013) reported that MgO produced at high temperatures has less reactivity and surface area than the MgO that is produced at lower temperatures of 700-1000^0 C. Cement is produced at temperature of 1450^{o}C, lime between 900-1000^{0}C and MgO between 700-800^{0}C. Therefore, the energy consumption for production of MgO

is less than the other two agents and it is more economic than lime and cement. Also, application of lime is limited to the soils with low clay content and low ambient temperature. Therefore, the benefits of using MgO in soil stabilization are not only in terms of low energy cost and positive environmental impact, but also in term of its high capacity for reabsorbing CO_2 of environment for carbonation reaction (Harrison, 2001, Al-Tabbaa, 2013 and Olajire, 2013). Therefore, MgO is a suitable alternative for cement as stabilizer agent. MgO is also used alone as a cementing agent for stabilization or as an additive in cement, lime or ground granulated blastfurnace slag (GGBS). The mixture of MgO with cement and fly ash is also used for remediation of contaminated soil (Iyengar and Al-Tabbaa, 2008). Vandeperre et al. (2008a and 2008b) studied the effect of MgO alone or mixture of MgO and cement on stabilization of a soil. They showed that the unconfined compressive strength of MgO-stabilized soil is dependent on the large pores that are present in the stabilized soil mass. They argued that the reaction of MgO produces larger pores than cement and therefore the strength and stiffness of sample is reduced significantly when MgO replaces cement as a stabilizing agent. Liska et al. (2008) and Liska and Al-Tabbaa (2009) showed that using MgO alone has advantages in terms of mechanical and durability performance and CO_2 sequestration in comparison with the mixture of cement and MgO. They reported that the carbonation of reactive MgO is very limited at ambient curing condition. In order to facilitate the carbonation process, forced carbonation by increasing the CO_2 concentration is needed. Yi et al. (2013a and 2013b) studied the usage of carbonation reaction of MgO for stabilization two types of soil by forced carbonation under pure gaseous CO_2. They used triaxial apparatus for applying CO_2 under desired pressure for forcing the carbonation of a soil that was mixed with

MgO. They showed that a soil stabilized with MgO can be highly carbonated in a few hours when it is placed under pressure of CO_2. The final attained strength of these samples would be similar to or higher than the samples that were stabilized with mixture of MgO and Portland Cement (PC) at curing time of 28 days.

A review of the literature shows that data on stabilization of soil using reactive MgO under forced carbonation is relatively rare. Yi et al. (2016) conducted forced carbonation of soil samples that were prepared at three different water contents and mixed with 15% MgO. They flowed CO_2 into the samples under pressure of 200 kPa at different periods (1.5, 3, 6 and 12 hours). However, they did not examine this method of stabilization considering the effects of different percents of MgO or different pressures of CO_2 (they only applied pressure of 200 kPa). It can be said that stabilization with MgO and forced carbonation is a sustainable and rapid soil stabilization method in civil Engineering projects. If a road is to be constructed on an unsuitable soil such as clay, it would be problematic and the soil should be improved before construction of the road. The improved soil should be resistant to large deformations due to repeated cyclic load or continuous loading. There are many methods for soil improvement involving chemical stabilization. In this work, chemical stabilization was studied by using cement and MgO as agents. The effect of forced carbonation in stabilization of soil with MgO was also investigated. Therefore, the aim of this work is to study the effect of forced carbonation under different CO_2 pressures and different durations of flow on samples prepared with different percents of MgO. The strength of these stabilized samples will be measured and compared with the results for samples made with cement or MgO alone with the same percent of stabilizing agent at different curing time. The mechanical properties of the

stabilized soils will be examined with the aid of SEM (Scanning Electron Microscopy) and XRD (X-ray diffraction) results.

Experimental Study

Material properties

The main materials that were used in this work were soil, cement and MgO. A brief explanation of these materials is presented below.

Soil

A clay soil was used in this work and was supplied by a local supplier. Grain size distribution test was carried out on samples of the soil according to ASTM D6913-04 and D7928-17 standards. The results showed that the soil was composed of 6% sand, 57% silt, and 27% clay. The consistency limits tests were conducted on samples of the soil according to ASTM D4318-10 standard. The results showed that the soil had a liquid limit (LL) and plastic limit of 70.0 and 25.0% respectively. The compaction test was conducted on the soil according to the ASTM D698-07e standard. The results showed that the optimum water content was 25.0% corresponding to maximum dry unit weight of 15.7 KN/m^3 as shown in Fig.1. The specific gravity of solids (G_s) was determined as 2.75 according to ASTM D854-14 standard. This soil was classified as clay with high plasticity (CH) according to the Unified Soil Classification System (USCS) with the aide of ASTM D2487-11 standard. Table 1 presents a summary of chemical properties of this soil. X-ray diffraction (XRD) tests were conducted on the samples of the soil. The XRD test was conducted by using a powder diffractometer D4 Discover (Bruker Corporation) with a Cu Kα source and wavelength of 1.54 angstrom (Å). Its slit width was 1.00 mm

and the counting time and step size were 1 sec and 0.02^0. The voltage and current of the apparatus were 40 kV and 40 mA, respectively.

Based on the XRD tests (Fig.2), the minerals of the soil were calcite, quartz and clay. The clay minerals of the soil were illite, kaolinite and montmorillonite.

Cement

Portland cement type 1 was used in this study. The specific gravity and Blain fineness of the cement were 3.15 and 4200 cm^2/g, respectively. Table 2 presents the physical and mechanical properties of the cement.

MgO

A commercial reactive MgO was acquired from a chemical supplier. Based on the information obtained from supplier, its chemical compositions were MgO, CaO, SiO_2, Fe_2O_3, Al_2O_3 equal to 94.2, 1.7, 0.85, 0.62, and 0.16%, respectively. Its molecular weight was 40.304 g/mol with specific gravity of 3.55 and specific surface of 250-300 m^2/g. The mean diameter size of its particles was 60 (μm).

Sample preparation

The cement and MgO contents used in the experimental program are defined as:

$$\rho_c = \frac{w_c}{w} \tag{1}$$

$$\rho_{MgO} = \frac{w_{MgO}}{w} \tag{2}$$

where ρ_c and ρ_{MgO} are cement and MgO contents and w_c, w_{MgO} and w are the weights of cement, MgO and natural air dried soil, respectively. The values of ρ_c and ρ_{MgO} were considered as 5, 10, 15 and 20% in the experimental tests. The air dried soil was mixed by hand with desired amount of cement or MgO. Then standard compaction tests were

conducted on the natural soil and mixture of soil and cement or MgO according to ASTM D 698-07e. The compaction curves, maximum dry unit weight and optimum water content were determined for the natural soil and the mixtures of soil with different percents of cement or MgO. The samples for forced carbonation and strength testing were compacted at maximum dry unit weight and optimum water content corresponding to each material.

Preparing the samples was done by weighting the soil and cement or MgO. They were mixed in a container and then water was added incrementally to these mixtures according to the optimum water content corresponding to compaction curve. The samples were mixed thoroughly. Static compaction was used for making the samples. The natural soil and mixtures of soil and cement or MgO were compacted in a special mould fabricated from steel. The mould used consisted of three sections, top collar, middle section and bottom collar. Each section was split vertically into halves (Estabragh et al., 2012). These sections were designed in a way that dismantling was easy and caused little disturbance to the compacted samples. The diameter and length of middle section were 50 and 100 mm, respectively. The mould was also provided with a piston that was used to compress the sample inside the mould in a compression frame. Before compaction the soil the internal walls of the mould were coated with lubricant in order to reduce the effect of friction. Compaction was done in three layers at the rate of 1.5 mm/min under a predefined load (determination of applied load was based on trial and error) until the maximum dry unit weight was achieved. The prepared soil-cement and soil-MgO samples were stored in a curing cabinet according to the ASTM D1632-07 standard for curing times of 7, 14, and 28 days.

Experimental tests

The laboratory tests including Atterberg limits, compaction and unconfined compressive strength (UCS) were conducted on the natural soil and mixtures of soil with different percents of cement or MgO according to the ASTM standards. UCS tests were also conducted on the samples that were made of soil and MgO that were subjected to the forced carbonation process under different pressures of CO_2 with concentration of 99.9% at different times. During the UCS tests, loading was continued on each sample until the failure of sample was observed. Two observations were considered as failure of a sample: (i) the observation of a clear failure plane or failure on the outside surface of sample such as crack (ii) the micro failure that was not observed but was implied by the loading gauge reading constant or decreasing load as the axial strain increased. The stress-strain curve was then established and the final strength of the sample was determined. A triaxial apparatus, as shown in Fig.3, was used for flowing CO_2 into the sample for the forced carbonation process. Each sample was set up in the triaxial apparatus according to the standard method that was proposed by Head (1986) for performing triaxial tests. The back pressure line connected a source of pure CO_2 to the bottom of sample. A gauge was installed between the source of CO_2 and bottom of sample for controlling the pressure of CO_2. The cell pressure was applied by using a constant pressure unit that was connected to the triaxial cell through a tube (Fig.3). After placing the sample in the cell of the triaxial apparatus it was filled with water and then the desired cell pressure was applied to the water in the cell by a constant pressure unit. CO_2 was flowed to the sample through the back pressure line. The difference in pressure between cell pressure and pressure of the CO_2 in the sample (back pressure) was kept at 50 kPa all the time. The tube that was

connected to the top of sample through top cap was placed under the water of a bowl to observe the flow of CO_2. By observing the flow of CO_2 the valve of this tube was closed. The inlet valve of back pressure was kept open to maintain the CO_2 at the desired pressure for a specific time in the sample. The applied pressures of CO_2 that were used in this work were 50, 100 and 150 kPa for duration of 4, 8, 12 and 24 hours for samples with different percents of MgO.

Scanning electron microscope (SEM) analysis was conducted on selected samples of natural and stabilized soil with MgO or cement to investigate their microstructures. The Apparatus used for testing was HITACHI model S-4160. The samples were grounded to small pieces and dried by using vacuum for a few days to remove their moisture. They were then placed on metal stubs, sputter coated by gold and then placed in the apparatus. XRD tests were also performed on the selected samples to identify the hydration products formed within the stabilized soil. Details of the apparatus used were explained in the previous section (natural soil behavior). The samples were grounded to particle sizes less than 125 μm and them used for XRD testing. The relative diffraction peaks of different hydration products formed in stabilized soil were identified using this test.

Results

The obtained results are described in the following sections:

Atterberg limits and compaction

Table 3 shows the results of Atterberg limits and standard compaction tests for the soil and mixtures of soil with different cement or MgO contents. As shown in this table, the values of LL, PL and PI for natural soil are 70, 25 and 45%. By adding 5% cement to the soil the values are changed to 79, 39 and 40%, respectively. There is an increase in the

values of LL and PL in comparison with the natural soil. By increasing the percent of cement to 10, 15 and 20 % the values of LL and PL are decreased in comparison with mixture of soil with 5% cement. It is also seen from this table that adding MgO to the soil causes increase in the values of Atterberg limits in comparison with the natural soil and the mixture of soil and cement at the same percent. For examples the values of LL, PL and PI for soil that was mixed with 5% MgO are 95, 43 and 52%, respectively that are more than those for the natural soil and mixture of soil with 5% cement. The results show that these values are decreased with increasing the percent of MgO (similar to cement).

It is seen from this table that the maximum dry unit weight and optimum water content for natural soil are 15.7 KN/m^3 and 25%, respectively. By adding 5% cement, the maximum dry unit weight and optimum water content (14.94 KN/m^3 and 23.6%) are decreased in comparison with the compaction parameters of the natural soil. The maximum dry unit weight and optimum water content for mixture of soil and MgO are decreased in comparison with the natural soil. It is observed from this table that by increasing the percent of MgO, the value of dry unit weight is decreased but there is no specific trend for changes of optimum water content with increasing the percent of MgO.

Uncofined compressive strength (UCS)

The maximum strength was obtained from the results of stress-strain curves for the natural soil and the soil stabilized with different percents of MgO or cement at different curing times. Fig.4 shows the variations of the maximum strength of stabilized soil with different percentages of cement or MgO against the curing time. As shown in this figure, by using 5 % cement as stabilizing agent, the strength of the natural soil (180 kPa) is changed to 632.5, 711.4, and 817 kPa at curing times of 7, 14, and 28 days, respectively.

For a given curing time, the strength is increased by increasing the percent of cement. Similar trends of variations of strength are also seen in this figure for different percents of used MgO. For example, for the samples stabilized with 15% MgO the final strengths at curing times of 7, 14, and 28 days are 1004, 1076, and 1254 kPa, respectively. It is resulted, from the obtained data, that for a constant percent of cement or MgO, the strength of the stabilized soil is increased by increasing the curing time. Also, at a constant curing time, the increase in the percent of MgO or cement causes increase in the strength of the stabilized soil (Fig. 4). By comparing the results in Fig.4 it is revealed that, for the same curing time and percent of agent, cement is more effective than MgO in increasing the strength of the soil. Fig.5 shows the final strength of the MgO stabilized soil against carbonation period for different percents of MgO and different applied CO_2 pressures. Fig.5a shows the final strength of the soil stabilized with 5% MgO under forced carbonation with different CO_2 pressures (0.5, 1.0 and 1.5 bar) at different carbonation periods. These results show that the final strengths of the samples are 414, 421, 441, and 479.4 kPa after forced carbonation with pressure of 1.5 bar for durations of 4, 8, 16, and 24 hours, respectively. It is resulted that forcing CO_2 into the sample increases the strength in short time. Fig.5 also shows that the final strengths of the samples with 5, 10, 15, and 20% MgO under 1 bar of CO_2 pressure for period of 4 hours, are 337, 506.3, 847.5, and 1172.15 kPa, respectively. It is resulted that, for a given CO_2 pressure and curing time, increasing in the percent of MgO increases the final strength of the soil.

Figs.6a and b present typical results of variation of percentage the mass increment of sample against carbonation period for the soil stabilized with MgO. Fig. 6a shows the

variation of mass increase of the soil stabilized with 15% MgO with carbonation period under pressures of 0.5, 1.0, and 1.5 bar. As shown in this figure, the majority of mass increase occurred within the first 8 hour of carbonation for each applied pressure and after that, the rate of mass increase was insignificant. From comparing the results in this figure, it can be concluded that, for a given carbonation period, the variations in the mass with carbonation pressure are not relatively small under the applied pressures. Fig.6b shows the variations of mass increase with carbonation period for the soil stabilized with 5, 10, 15, and 20% MgO at applied pressure of 1.5 bar. As shown in this figure, for each percent of MgO, the majority of increase in mass occurred within the first 8 hours of carbonation and after that the rate of increase was small. Fig.6b also shows that, at 24 hours of carbonation, the mass increment is 4.95% for 5% MgO and it is changed to 6.6% for 20% MgO. It can be concluded that the degree of carbonation is dependent on the percent of used MgO.

Scanning electron microscopy (SEM)

The microstructure of the sample was studied through scanning electron microscopy (SEM). Fig. 7a shows the SEM image of natural soil that is composed of particles with different sizes without any bonding between them. Typical images of soil treated with 10% MgO at curing times of 0, 7 and 14 days are shown in Figs. 7b, c and d, respectively. No hydration products are observed at curing times of 0 and 7 days in the test sample (Figs. 7b and c) but brucite, that is one of the hydration products, is seen in Fig.7d at the pores between particles that interconnects them. The SEM images in Figs. 7b, c and d show uncarbonated microstructures for samples that were subjected to natural curing. It may be that, due to the low amount of CO_2 in the air, natural curing takes place at much

slower rate than accelerated carbonation where CO_2 concentration was 20% and 28 days is a short period of time for carbonation to occur under natural condition (Unluer and Al-Tabbaa, 2013). Fig.8 shows the SEM image of soil stabilized with 10% MgO by forced carbonation at pressures of 0.5, 0.5 and 1 bar for 8, 24 and 8 hours, respectively. As shown in this figure, nesquehonite that is made of carbonation the brucite is seen between particles of the soil. The soil particles are connected to each other through a network of nesquehonite crystals which results in a rapid increase in strength of the stabilized soil. Fig.8a and b show the results for carbonation pressures of 0.5 and 1 bar for the same period (8 hr). The pores between the particles are smaller in Fig.8b than Fig.8a. It can be concluded that increasing pressure of carbonation increases the rate of carbonation in the sample. Comparison of the results in Figs.8a and 8c shows that, at the same pressure of CO_2, increasing the period of carbonation is effective in producing the nesquehonite crystals. It is evident from the SEM images of 8 and 12 hours for carbonated MgO stabilized soil that the soil particles are interconnected by a modified extensive network of nesquehonite crystals that are responsible for stabilization and rapid increase in strength of soil mass. The chemical reactions that occur between MgO and CO_2 during hydration are as follows (as used by Yi et al., 2016):

$$MgO + H_2O = Mg(OH)_2 \text{ (brucite)} \quad (3)$$

$$Mg(OH)_2 + CO_2 + 2H_2O = MgCO_3, 3H_2O \text{ (nesquehonite)} \quad (4)$$

$$5Mg(OH)_2 + 4CO_2 + H_2O = Mg_5(CO_3)(OH)_2, 5H_2O \text{ (dypingite)} \quad (5)$$

$$5Mg(OH)_2 + 4CO_2 = Mg_5(CO_3)_4(OH)_2, 4H_2O \text{ (hydromagnesite)} \quad (6)$$

Initially, MgO reacts with pore water and produces $Mg(OH)_2$. $Mg(OH)_2$ precipitates if the concentrations of Mg^{-+2} and OH^{-1} ions are enough in pore water (Li and Yi 2019). Then

the CO_2 that is introduced to the soil is dissolved in the pore water and produces the ions CO_3^{-2} and H^+. CO_3^{-2} and Mg produce $MgCO_3$ which participates between particles. If the initial concentrations of these materials are high, then nesquehonite, dypingite and hydromagnesite are formed and participated that cause binding of the particles. Unluer and Al-Tabbaa (2012) reported that the dense formation of nesquehonite produced higher strengths than similar mixes where dypingite or hydromagnesite was the main component forming after the carbonation process. From the micrographs shown in Fig.8, the shape of the products due to carbonation is similar to those that were reported by Unluer and Al-Tabbaa (2013).

Fig.9 illustrates the changes in the microstructure of soil stabilized with 10% cement at different curing times. No hydration products are observed in the samples at curing times of 0 and 7 days. Fig.9c shows that after 14 days more hydration products were formed and the spaces between the particles were filled with them which led to increasing the strength of the soil. These hydration products (shown in Fig.9c) are observed as needle-shaped (ettringite), hexagonal plate-shaped (portlandite) and gel-like (CSH). The obtained results are similar to the results that were presented by Yi et al. (2016) and Liska et al. (2008). As shown in the figure, the hydration products of cement cannot be seen for curing times of 0 and 7 days. Jin et al. (2015) explained that the effect of binder composition on the microstructure is not easy to be determined because of (i) the presence of soil particles, especially soft kaolin clay particles, which form a complex microstructure with specific minerals that are difficult to be identified; and (ii) the amorphous nature of the formed gel which intermixes together and has no specific form and morphology.

X-ray diffraction (XRD)

Fig.10. presents the XRD diffractograms of the stabilized soil with 10% MgO at different curing times and forced carbonation for period of 24 hours under 1 bar pressure. As shown in Fig.10a, for the stabilized soil at curing time of 0, no peaks of hydration products are detected. It is possible that some of these products may have formed in the soil mass but their peaks are coincided with the peaks due to the other minerals of the soil. Fig.10b shows a number of peaks detected for brucite (that is formed from hydration of MgO) in the soil at curing time of 7 days. The peaks due to the other hydration products were not detected. A similar observation is made in the results for the soil stabilized at 14 days of curing. It can be said that carbonation in air is not fast to produce other kinds of hydrated carbonates after 14 days (Fig.10c). It is possible that they are formed in the soil mass but the peaks of them are coincided with other peaks of this diffractogram. Fig.10d presents the XRD diffractograms of stabilized soil with 10% MgO under carbonation pressure of 0.5 bar for 24 hours. As shown in this figure, the peaks of brucites have disappeared but peaks of hydromagnesite and nesquehonite are seen after 24 hours. Dypingate may have been produced during the hydration of MgO and its peak may have overlapped with hydromagnesite.

Figs.11a and b illustrate the XRD diffractograms of stabilized soil with 10% cement at curing times of 7 and 14 days. As shown in these figures, no peaks due to ettringite, portlandite, CSH and CAH (that are hydration products of cement) are detected but a substance by the name of Gismondine (CASH) is detected in both conditions. The chemical formula for Gismondine is $CaAl_2Si_2O_8$, $4H_2O$ (Hydrated Alumine Silicate).

However, there are many overlapping peaks that pose a problem in identifying each one of the hydrated products of cement separately by XRD analysis.

Discussion

The clay soil surface carries negative charges and they can attract cations and the positive charge sides of molecules of water from water that surrounds these clay particles. It makes a layer of water that is bonded to the surfaces of clay particles and is known as diffuse double layer (DDL). The concentration of cations in this layer of water is high at the surface of particles and it is exponentially reduced with increasing the distance from particle surface (Cernica, 1995). Forces in the form of attraction or repulsion can be formed between the DDL of adjacent clay particles. Repulsion is occurred between two DDLs with the same charge and attraction with different charges. The net force influences the structure of soil so; if it is repulsion the structure is dispersed and if it is attraction, the structure is flocculated. Clay particles have cation exchange behavior, so, lower positive valence of elements can be replaced with existing higher positive valence of element in the system of clay and water (Mitchell and Soga, 2005). These cations, attached to the surface of clay particles are called exchangeable cations as they can be substituted with other cations (Mitchell and Soga, 2005). The total exchange of cations is termed cation exchange capacity (CEC). The cation exchange capacity influences the properties of soil.

The results of Atterberg limits (Table 3) show that by adding 5% cement to the soil the values LL and PL are increased in comparison with natural soil. Increasing the percent of cement causes decrease in the values of LL and PL in comparison the soil with 5% cement. Adding MgO to the natural soil causes changes to the Atterberg limits that

follow similar trends to the cement. The results show that at a constant percent of MgO and cement, the effect of MgO in increasing these parameters is more than cement. The mineralogy of clay, cation exchange and pH of pore water are effective in the variations of Atterberg limits (Croft, 1967). Phani Kumar and Sharma (2004) and Kumar et al. (2007) found similar results when a clay soil was mixed with fly ash. Specific surface of MgO is more than cement, therefore, it can absorb more water than cement which causes increase in the values of Atterberg limits in comparison with cement. These results are consistent with the results that were reported by Liska et al. (2008) who stated that, in general, MgO exhibits considerably higher water demand for its standard consistency than Portland cement.

The maximum dry unit weight for soil-cement and soil-MgO is less than natural soil and the dry unit weight of soil-MgO is more than soil-cement (Table 3). The maximum dry unit weight is increased by increasing the percent of cement but for MgO it is decreased. Fig.12 shows the variations of void ratio with the percentage of MgO used for stabilization. As shown in this figure, by increasing the percent of MgO, the void ratio is increased. This could be because MgO produces larger pores in the soil mass than cement. These results are in agreement with the findings that were reported by Vandeperre et al., (2008a and b). The variations of optimum water content have no specific trend for both agents (cement and MgO).

Fig.4 shows that the strength of soil-cement is increased by increasing the percent of cement or curing time. These are important factors in stabilization of soil as indicated by Bahar et al. (2004) and Khattach and Alrashidi (2006). The increase in the strength is due to the hydration, ion exchange, and pozzolanic reactions. In the hydration process,

cement absorbs the free water that exists between the soil particles and Ca^{+2} ions are released. Therefore, in the ion exchange a number of ions such as Na^{+} and K^{+} are replaced by Ca^{+2} ions. This exchange of ions causes reduction in the thickness of DDL and results a flocculated structure in the soil mass. In the new structure, the voids between particles are reduced and this increases the strength of the soil mass (Broms, 1986). During hydration the pozzolanic reaction occurs by producing calcium hydroxide and a gel that is called tobormite gel (Broms, 1986). This gel is responsible for the final cementitious bonding in the stabilized soil mass. During hydration, the pH of the pore fluid is increased and it causes the solution of acidic silica and alumina that exist in the soil mass. Chemical reaction also occurs between these products and produces cementitious materials such as calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) in the soil mass. These gels bind the soil particles together (Fig.9c) and form a hard structure so that particles of soil can no longer slide over each other. These reactions cause increase in the strength of the soil. Therefore, the increase in the strength of soil-cement with time is mainly due to pozzolanic reaction. These results are in agreement with the results that were reported by Kézdi (1979) and Mindess and Young (1981). Fig.4 also shows that the strength of soil stabilized with MgO is increased with increasing the percent of MgO and curing time. When MgO is added to the soil as a binder, the hydration process is begun by absorbing the free water between particles. The rate of hydration, of MgO is similar to that of cement (Vandeperre et al., 2006). During the initial stage of this process, exchange ions occurs between Mg^{+2} and a number of ions. The exchange of ions influences the thickness of DDL and causes a change in the structure of the soil. During hydration MgO is also changed to $Mg(OH)_2$ that is

magnesium hydroxide and is called brucite (eq. 3). When brucite is subjected to the curing process, it can react with CO_2 and water. This results in increase in the strength due to the production of hydrated magnesium carbonates. The produced materials are, for example, nesquehonite ($MgCO_3$,$3H_2O$), hydromagnesite ($4MgCO_3$, $Mg(OH)_2$, $4H_2O$) and dypingite ($4MgCO_3$ $Mg(OH)_2$, $5H_2O$) as shown in eqs. 4-6. However, by carbonation of MgO, magnesium carbonate is produced that is an important source for production of magnesia. Unluer and Al-Tabbaa (2011 and 2012) indicated that between the produced materials such as nesquehonite, hyromagnesite and dypingite, the strength of nesquehonite is higher than the other materials. This could be due to the growth of fibrous and acicular crystals in nesquehonite as reported by Lanas et al. (2006). Therefore, for a specific percent of MgO used as binder, stabilization is dependent on the availability of free water and CO_2 for carbonation process and it is completed by passing the time. The results (Fig.4) show that at a specific curing time, the strength is increased with increasing the percent of used MgO. It can be said that when the percent of used MgO is increased, more carbonation products are produced and this increases the strength of the soil mass. It is observed from Fig.4 that at the same percent of cement and MgO and for a specific curing time, the achieved strength due to cement is more than MgO. It can be said that the materials that are during the hydration of cement are stronger than those produced by hydration of MgO and as a result cement stabilized soil is stronger than MgO stabilized soil. Vandeperre et al. (2008a and b) indicated that MgO produces larger pores in the soil mass than cement. This results in lower strength than soil-cement at the same percent and curing time as shown in Fig.4. Vandeperre et al. (2008a) also indicted that more solid is formed during hydration of 1g MgO than 1g Portland cement but MgO

is less effective than cement in filling the free space and removing large pores of soil mass. They explained that is due to the formation a crystalline product whereas cement makes a microporous gel. Fig.5 shows the final strength of the samples after a specific time of forced carbonation the samples under a specific pressure of CO_2. As shown in Fig.5a, the final strength of the sample stabilized with 5% MgO under pressure of 0.5 bar after periods of 4 and 8 hours is 236 and 288 kPa but its strength reached 261 kPa after curing time of 7 days (Fig.4). This indicates that the forcing of CO_2 causes increase in the strength at a very short time. This could be due to the increase in the adsorption of CO_2 by mixture of soil and MgO and acceleration in the production of hydration products which results in greater binding of soil particles with carbonation products and reduction in the porosity of stabilized soil. It is observed from this figure that by increasing the pressure of forcing CO_2 the strength of sample is increased. For example, as shown in Fig.5a, for 4 hours of enforcing CO_2 in the samples the strengths of samples are 236, 337, and 414 kPa for CO_2 pressures of 0.5, 1, and 1.5, bar respectively. It is resulted from comparing the results in Figs.5a and b that at constant pressure and time of forcing the CO_2 into the sample, the strength of the soil increases by increasing the percent of MgO. For example, for the sample mixed with 5% MgO, the strength of sample after a period of 4 hours of enforcing CO_2 under pressure of 0.5 bar is 236, but under the same conditions, the strength of the sample that was made with 10% MgO reaches to 324 kPa. It is resulted that during the carbonation of mixture of soil-MgO, the CO_2 gas is absorbed and solidifies the soil mass. Therefore, both MgO and CO_2 can be considered as binders. These results are consistent with the results that were reported by Yi et al. (2016 and 2013a and b).

In this study, the stabilization soil was considered in two groups. In the first group, the stabilization was conducted with different percents of cement or MgO and the strength of the soils was determined using UCS tests at different curing times. In the second group the stabilization was done by MgO and carbonation by CO_2 in a triaxial cell with a confining pressure for various times and different gas pressures. These different methods of stabilization in the laboratory provide information for comparison of the different method of stabilization of soil. The price of the MgO that was used in this work was more than cement. Without considering and comparing the environmental impacts of MgO and cement, cement may appear to be more economic than MgO. However, if the environmental cost of producing cement is considered, then MgO might be the preferred solution. The present study confirms that the use of MgO and forced carbonation is a sustainable and rapid method for stabilization of soils, as it can be achieved in a few hours and result in a high strength in the soil. If the needed CO_2 is provided from waste CO_2 that is produced in industrial factories, it can lead to reduction in the cost of CO_2 (and stabilization) and can address the important environmental problem of reducing CO2. On the other hand, if the relatively low percent of MgO is suggested for stabilization of soil through forced carbonation, the cost of MgO and cement will be close to each other provided that the CO_2 is obtained from industrial sections. It can be said that the cost of this method may be similar to the conventional cement stabilization of soil. More detailed environmental and economic studies are required for a definite conclusion.

This method can be used for ground improvement and stabilization and solidification of contaminated soils (Yi et al., 2013a). In practice, mixing of clay soil with cement or MgO

in the field to achieve a uniform mixture could be a problem because of high plasticity of clay soil. Zhang et al. (2003) developed a fiber-soil mixing process in the field. However, with development of construction techniques it will be possible to use of MgO and CO_2 for stabilization of clay soils in the field. After mixing soil and MgO, the CO_2 can be injected to the soil with desired pressure through a perforated pipe, similar to soil vapor extraction or air sparing system (Yi et al., 2016). However, more study is needed to use this method correctly in the field.

Conclusion

A number of tests were conducted on samples of clay soil stabilized with different percents of cement or MgO at different curing times. Also, a number of tests were carried out on soil stabilized with MgO that was subjected to forced carbonation by flowing CO_2 under different pressures and times. The effects of cement, MgO and flowing of CO_2 on stabilization of the clay soil were studied. The main conclusions drawn from this study are as follows:

- MgO can increase the strength of soil and the amount of increase in strength is dependent on the percent of used MgO and curing time.
- The trend of variations of strength for MgO is similar to cement. However, for the same percent of MgO and cement and the same curing time, the amount of increase in strength for MgO is less than cement.
- Forced carbonation of soil-MgO by flowing of CO_2 into the soil increases the strength of the mixture and the amount of increase in strength is a function of the pressure and duration of the flow. For a given pressure and duration of the forced

carbonation, the strength and the carbonation processes are enhanced by increasing the percent of MgO.

- Stabilization of soil by MgO and forced carbonation is a rapid and sustainable stabilization method in comparison with cement. A lower percent of MgO can be used in this method in comparison with cement to achieve similar strength in the stabilized soil.

References

Al-Tabbaa, A., 2013. *Reactive magnesia cement*. In Eco-efficient concrete, part 4, chapter 19. edited by Pacheco-Torgal, S. Jalali, J. Labrincha, and V.M. John, Woodhead Publishing Cambridge, UK.

ASTM, 2004. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2007. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2007e. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2008. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2010. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2011. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2014. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

ASTM, 2017. Annual book of ASTM standards, soil and rock. West Conshohocken, PA: American Society for testing Materials.

Bahar, R., Benazzoug, M., Kenai, S., 2004. Performance of compacted cement stabilized soil. *Cement & Concrete Compos*ities, **24**(7), 811-820.

Broms, B. B., 1986.*Stabilization of Soft Clay with Lime and Cement Columns in Southeast Asia* :Applied Research Project RP10/83 . Nanyang Technical Institute, Singapore.

Cernica, J.N., 1995. Geotechnical Engineering: Soil Mechancs, John Wiley & Sons, Inc., USA.

Chew, S.H., Kamruzzaman, A.H.M., Lee, F.H., 2004. Physicochemical and engineering behavior of cement treated clays. *Journal of Geotechnical and Geoenvironmental Engineering*, **130** (7), 696-706.

Croft, J.B., 1967. The influence of soil mineralogical composition on cement stabilization. *Geotechnique*, **17**, 119-135.

Estabragh, A.R., Khatibi, M., Javadi, A.A., 2016. Effect of cement on treatment of a clay soil contaminated with glycerol. *Journal of Materials in Civil Engineering,* **28** (4), 04015157-1~~, 10~~

Estabragh, A.R., Namdar, P. Javadi, A.A., 2012. Behavior of cement-stabilized clay reinforced with nylon fiber. *Geosynthetics International*, **19** (1), 85-92.

Harrison, J., 2001. *Reactive magnesium oxide cements*. International Patent. WO/2001/055049.

Head, K.H., 1986. *Manual of soil laboratory testing*. Pentech Press, London, UK

Higgins, D., 2007. Briefing: GGBS and sustainability. *Proceeding of the Institution of Civil Engineers*, *Construction Materials*, **160** (CM3), 99-101.

Iyengar, S.R., Al-Tabbaa, A., 2008. Application of two novel magnesia-based cements in the stabilization/ solidification of contaminated soils. *In:Proceeding:ASCE (Ed.).*

GeoCongress: the challenge of sustainability in the Geoenvironment. Reston VA, USA, Orleans, 716-723.

Jin, F., Gu, K., Al-Tabbaa, A., 2015..Strength and hydration properties of reactive MgO activated ground granulated blastfurnace slag paste. Cement & Concrete Composites, **57**, 8-16.

Kézdi, Á., 1979. *Stabilized earth roads*. Elsevier publisher.

Khattak, M.J., Alrashidi, M., 2006. Durability and mechanistic characteristics of fiber reinforced soil-cement mixtures. *International Journal of Pavement Engineering,* **7**, 53-62.

Kumar, A., Walia, B.S., Bajaaj, A., 2007. Influence of fly ash, lime and polyester fibers on compacted and strength properties of expansive soil. *Journal of Materials in Civil Engineering*, **19** (3), 242-248.

Lanas, J., Bernal, P., Bello, M.A., Alvarez, J.I., 2006. Mechanical properties of masonry repair dolomitic lime-based mortars. *Cement and Concrete Res*earch, **36**, 951-960.

Li, W., Yi, Y., 2019. Stabilization/solidification of lead and zinc-contaminated soils using MgO and CO_2. *Journal of CO_2 Utilization*, **33**, 215-221.

Liska, M., Vandeperre, L.J., Al-Tabbaa, A., 2008. Influence of carbonation of magnesia-based pressed masonry units. *Advances in Cement Res*earch, **20** (2), 53-64.

Liska, M., Al-Tabba, A., 2009. Ultra-green construction:reactive magnesia masonry products. *Proceeding of the Institution of Civil Engineers*, *Waste and Resource Management,* **162** (4), 185-196.

Mindess, S., Young, F.J., 1981. *Concrete*, Englewood Cliffi N.J. Prentice-Hall.

Mitchell, J. K., Soga, K., 2005. *Fundamentals of soil behavior (3rd Ed)*. Hoboken: John Wiley & Sons.

Olajire, A.A., 2013. A review of mineral carbonation technology in sequestration of CO_2. *Journal of Petroleum Science and Eng*ineering, **109**, 364-392.

Phani Kumar, B.R., Sharma, R.S., 2004. Effect of fly ash on engineering properties of expansive soils. *Journal of Geotechnical and Geoenvironmental Eng*ineering, **130** (7),764-767.

Puppala, A.J., Wattanasanticharoen , E., Punthutaecha, K., 2003. Experimental evaluations of stabilization methods for sulfate-rich expansive soils. *Proceeding of the Institution of Civil Engineers*, *Ground Improv*ement, **7** (1), 25-35.

Unluer, C., Al-Tabbaa, A. 2011. Green construction with carbonating reactive magnesia porous blocks. Effect of cement and water contents. *In: Proceeding of the 2nd International Conference & Environmental Construction Exhibition*, Dobai.

Unluer, C., Al-Tabbaa, A. 2012. Effect of aggregate size distribution on the carbonation of reactive magnesia based porous blocks. *In:Proceeding of the 18th Annual International Sustainable Development Research Conference*, Hull, UK.

Unluer, U., Al-Tabba, A., 2013. Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements. *Cement and Concrete Res*earch, **54**, 87-97.

Vandeperre, L.J., Liska, M., Al-Tabbaa A., 2006. Mixtures of pulverized fuel ash, Portland cement and magnesium oxide: strength evolution and hydration products. *In:Proceeding of the 6th International Conference on the Science and Engineering*

of Recycling for Environmental Production, Yugoslav Engineering Academy, Belgrade, 539-550.

Vandeperre, L.J., Liska, M., Al-Tabbaa, A., 2008a. Microstructures of reactive magnesia cement blends. *Cement & Concrete Compos*ities, **30**, 706-714.

Vandeperre, L.J., Liska, M., Al-Tabbaa, A., 2008b. Hydration and mechanical properties of magnesia, pulverized fuel ash and portland cement blends. *Journal of Materials in Civil Eng*ineering, **20** (5), 375-383.

Yi, Y., Liska, M., Akinyugha, A., Unluer, C., Al-Tabba, A., 2013a. Preliminary laboratory-scale model auger installation and testing of carbonated soil- MgO columns. *Geotechnical Testing J*ournal, **36** (3), 384-393.

Yi, Y., Liska, M., Unluer, C., Al-Tabba, A., 2013b. Carbonating magnesia for soil stabilization. *Canadian Geotechnical J*ournal, **50** (8), 899-905.

Yi, Y., Lu, K., Liu, S.m Al-Tabba, A., 2016. Property changes of reactive magnesia-stabilized soil subjected to forced carbonation. *Canadian Geotechnical J*ournal **53**, 314-325.

Zhang, Z., Farrag, K., Morvant, M., 2003. *Evaluation of the effect of synthetic fibers embankments*. FHWA/LA.03/373. Louisiona Transportation Research Center, Baton Rouge, LA, USA, 7-19.

Table. 1 Chemical composition of soil

Chemical component	Amount	Chemical component	Amount
pH	7.78	Cl^- (meq/L)	23.75
EC[a] (dS/m)	8.24	HCO_3^- (meq/L)	6.25
Na^+ (meq/L)	91.4	SO_4^{2-} (meq/L)	80.34
Ca^{2+} (meq/L)	25.11	CO_3Ca (%)	5.2
Mg^{2+} (meq/L)	4.65	O.C.[b] (%)	0.10

a-Electrical Conductivity
b-Organic content

Table. 2 Properties of cement

Properties	Standard designation	Value
Normal consistency (%)	ASTM C 187-10	28.2
Primary setting time (min)	ASTM C 191-08	92
Final setting time (min)	ASTM C 191-08	218
Compressive strength (MPa) 7days	ASTM C 109-08	26.2
Tensile strength (MPa) 7 days	ASTM C 190-85	2.7
Flexure strength (MPa) 7 days		5.3

Table.3 Atterberg limits and compaction parameters for natural soil and soil after adding different percents of cement or MgO

Material	LL (%)	PL (%)	PI (%)	$\gamma_{d(max)}$ (KN/m^3)	$w_{(opt)}$ (%)
Soil	70	25	45	15.7	25.0
Soil+5% cement	79	39	40	14.95	23.6
Soil+10% cement	77	38	39	15.1	23.0
Soil+15% cement	74	36	38	15.6	19.3
Soil+20% cement	71	35	36	15.7	20.0
Soil+5% MgO	95	43	52	15.3	17.7
Soil+10% MgO	91	41	50	14.47	16.7
Soil+15% Mgo	88	39	49	14.2	18.0
Soil+20% MgO	87	37	50	14.1	19.0

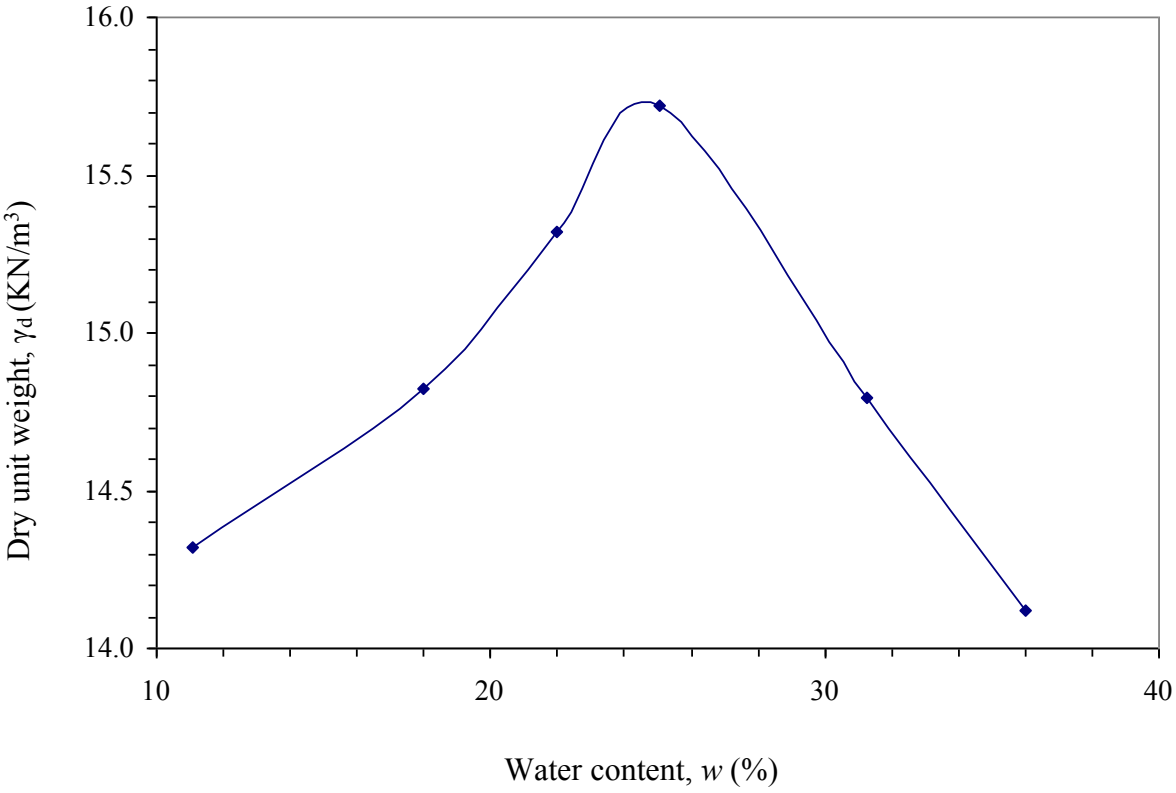


Fig.1. Compaction curve of natural soil

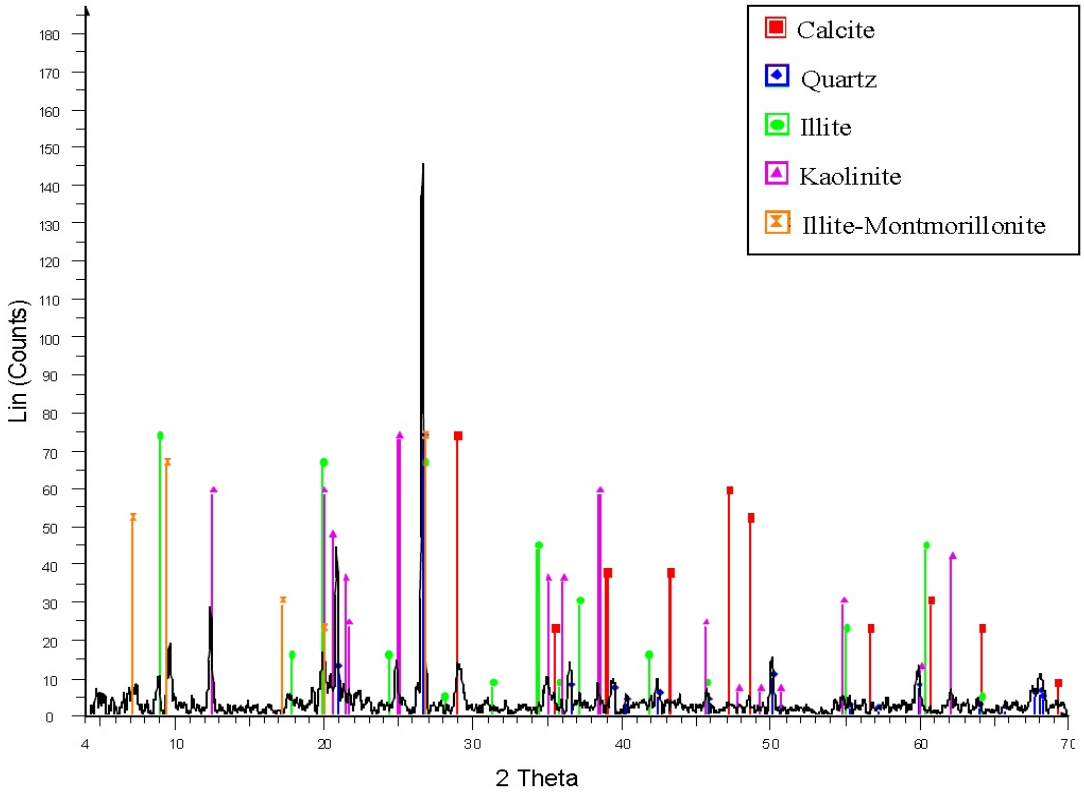
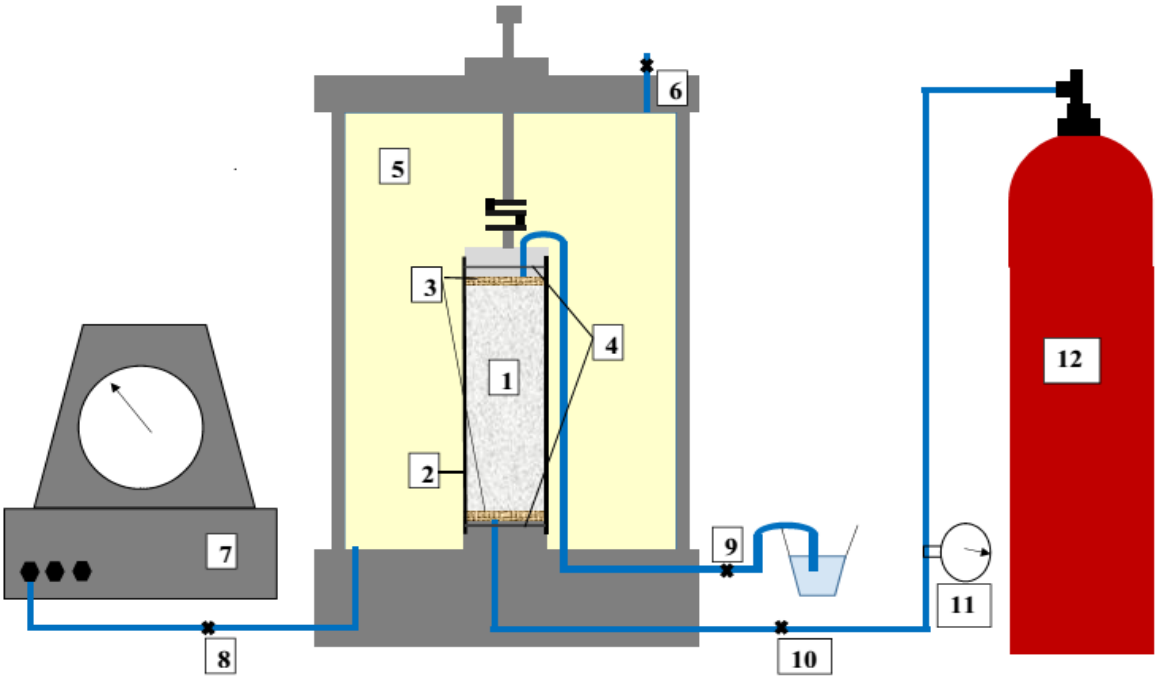


Fig.2. XRD diffractogram for natural soil



1-Sample,	4- O ring	7- Constant pressure	10- CO_2 inlet
2-Membrane	5- Cell	8- Confining pressure	11- Gauge
3-Porous stone	6- Air valve	9- CO_2 out flow	12- Source of CO_2

Fig.3. Layout of triaxial apparatus used for MgO-stabilization of soil by forced carbonation

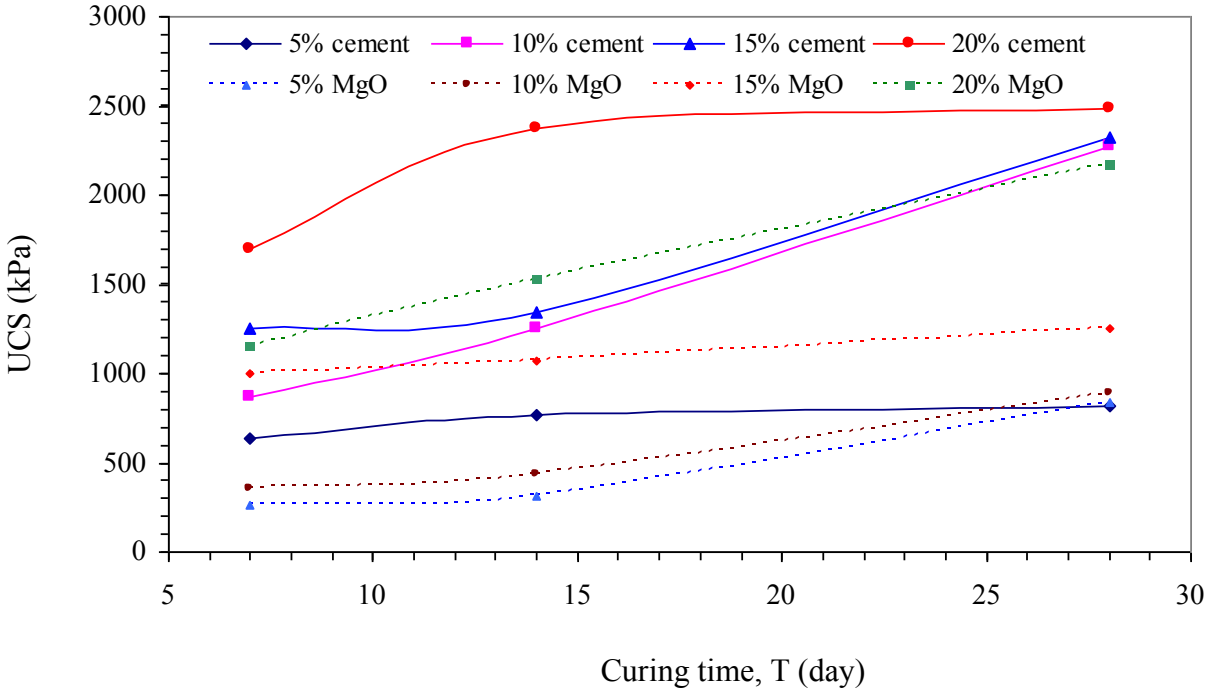
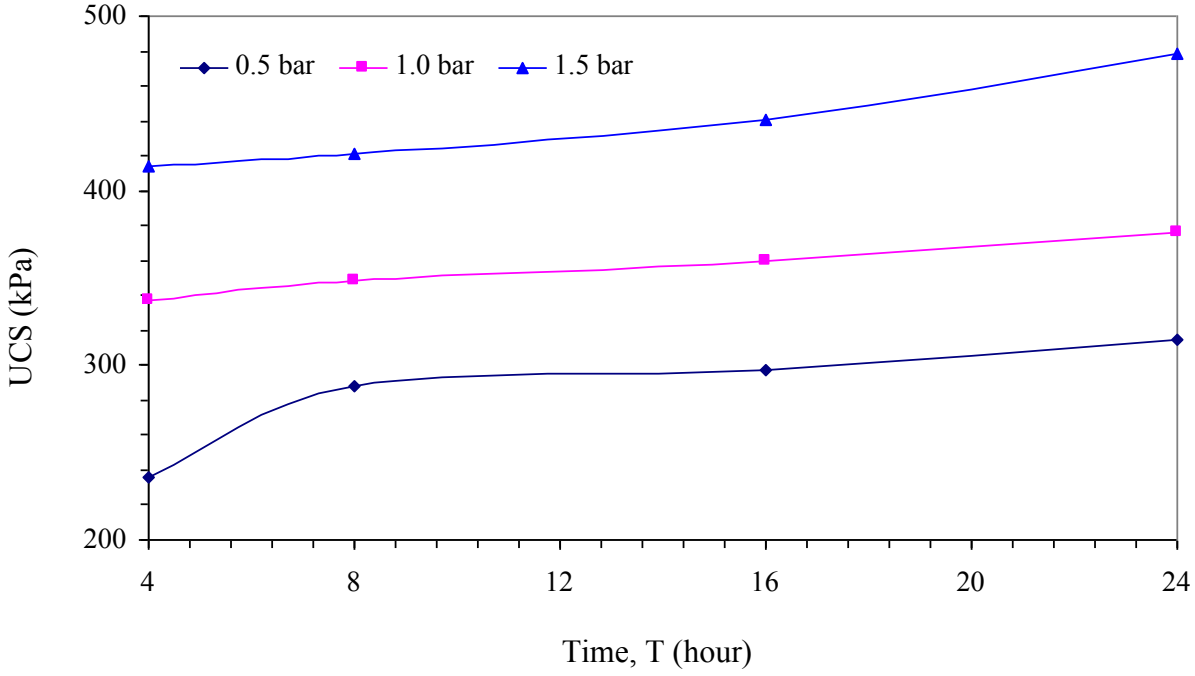
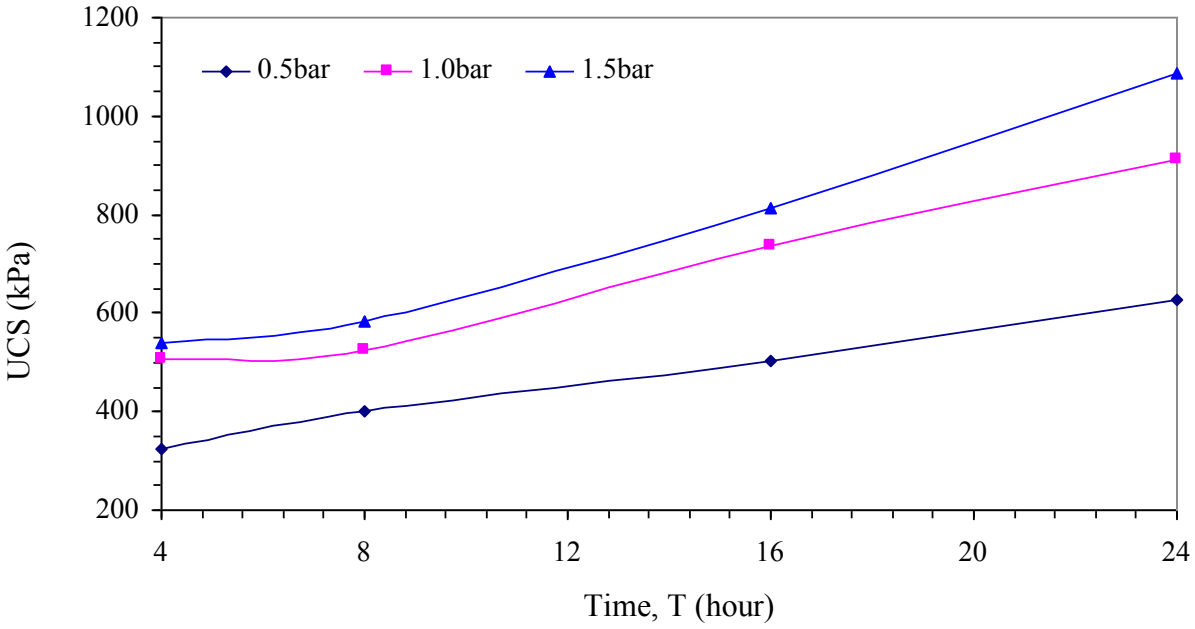


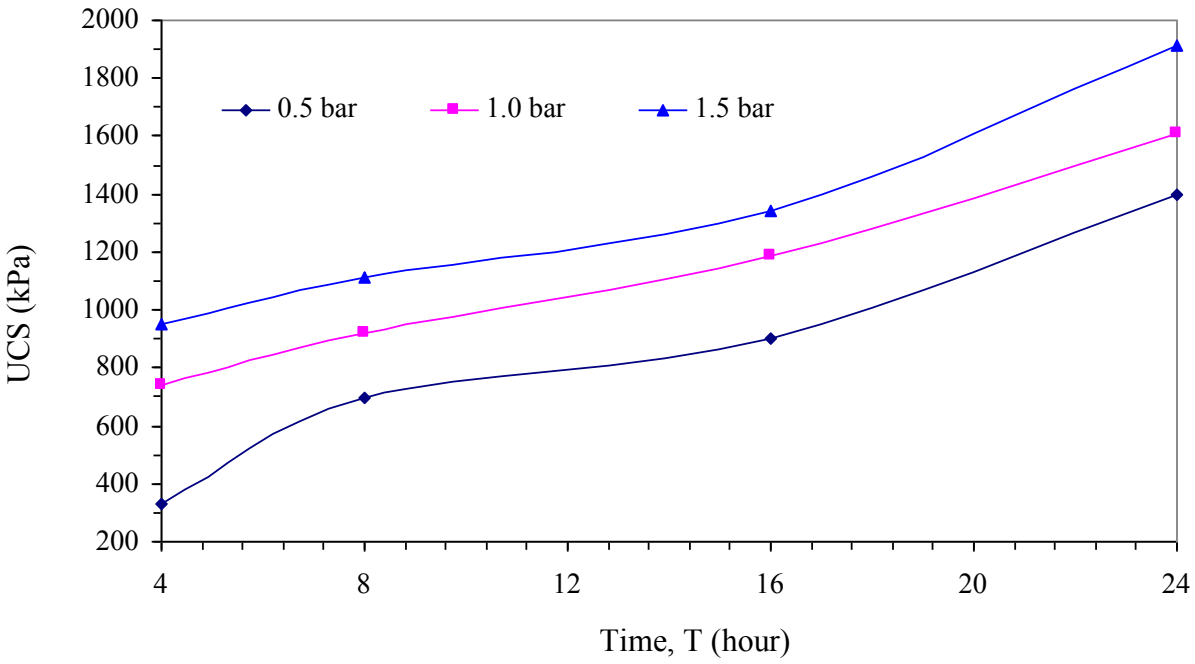
Fig.4. Variation of compressive strength with curing time for soil-cement and soil-MgO with different percentages of cement and MgO



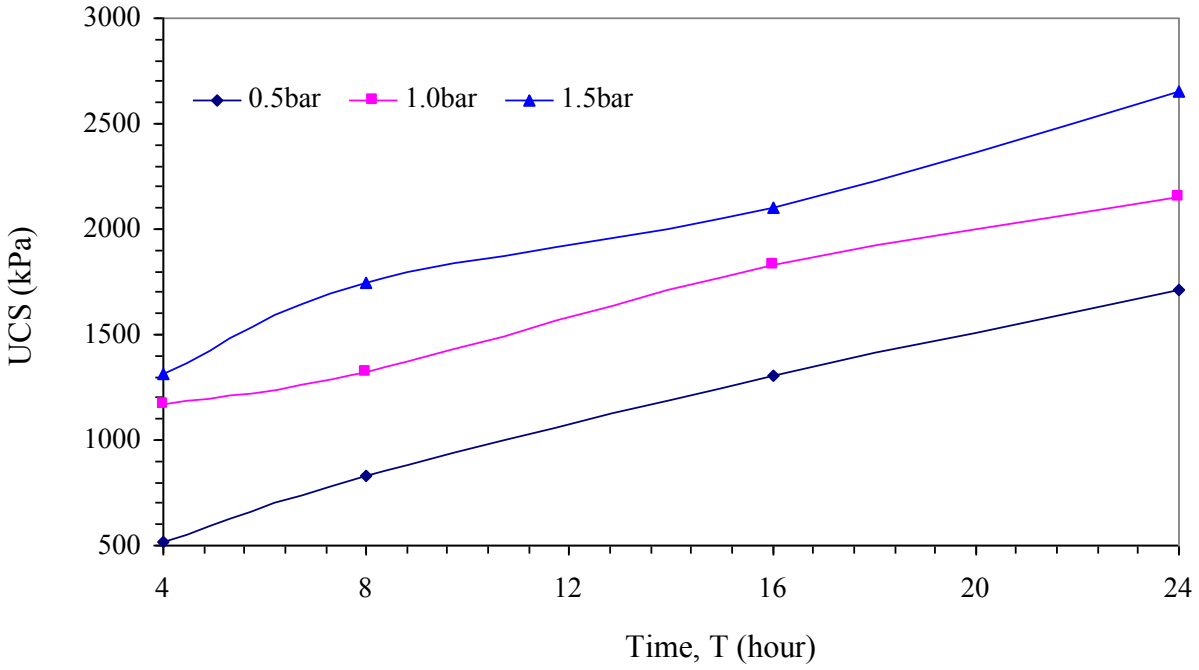
(a)


0.5bar
1.0bar
1.5bar
UCS (kPa)
Time, T (hour)
200
400
600
800
1000
1200
4
8
12
16
20
24

(b)

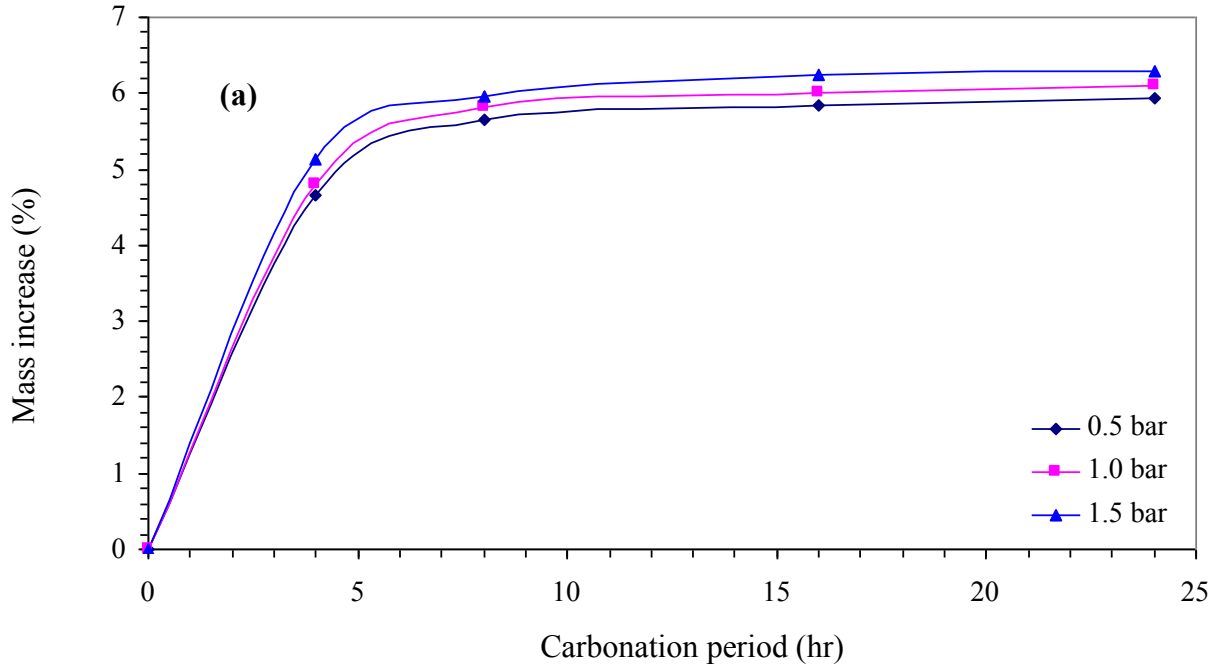

0.5 bar
1.0 bar
1.5 bar
UCS (kPa)
Time, T (hour)
200
400
600
800
1000
1200
1400
1600
1800
2000
4
8
12
16
20
24

(c)



(d)

Fig.5. Variation of compressive strength with time for soil with different percentages of MgO under different pressures of CO_2 . **(a):** soil-5% MgO, **(b):** soil-10% MgO, **(c):** soil-15% MgO, **(d):** soil-20% -MgO



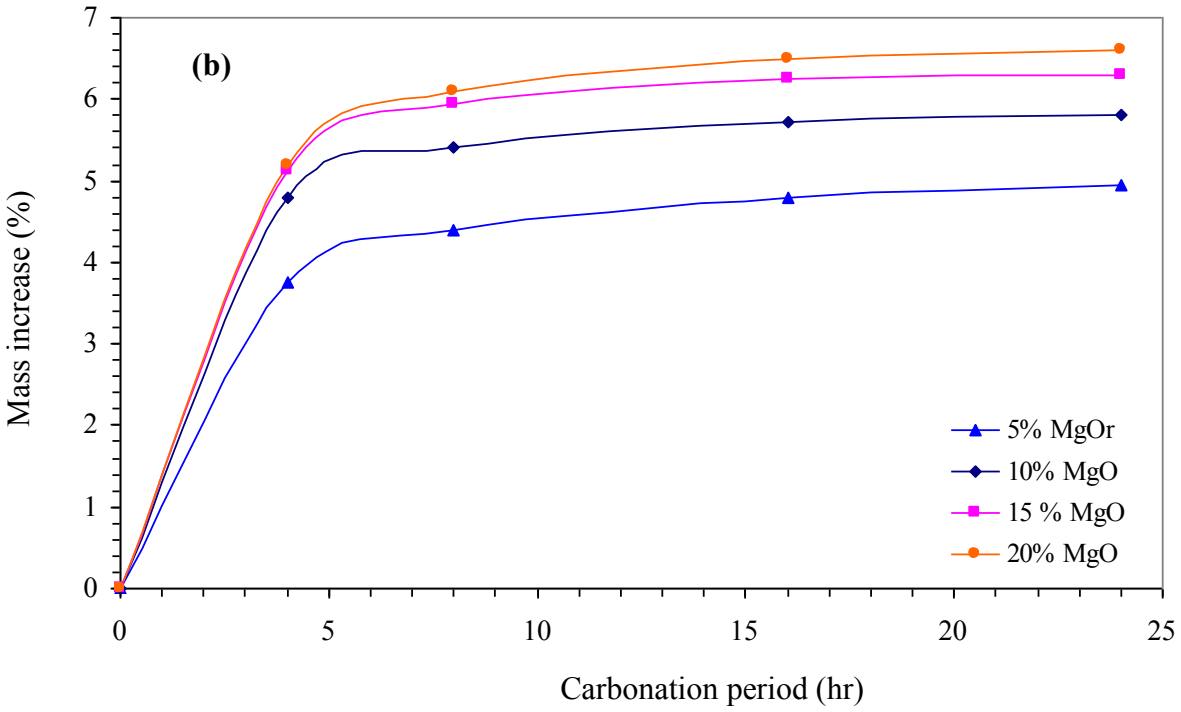
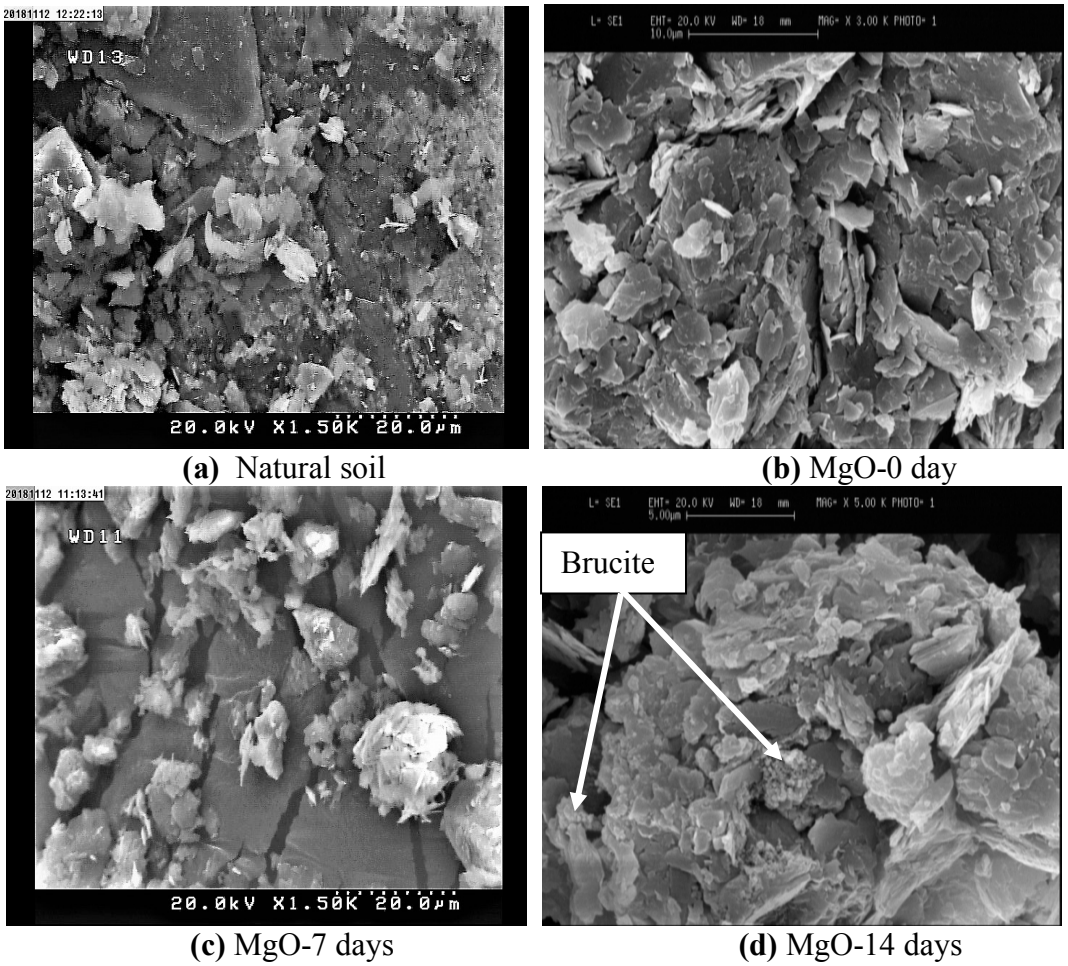


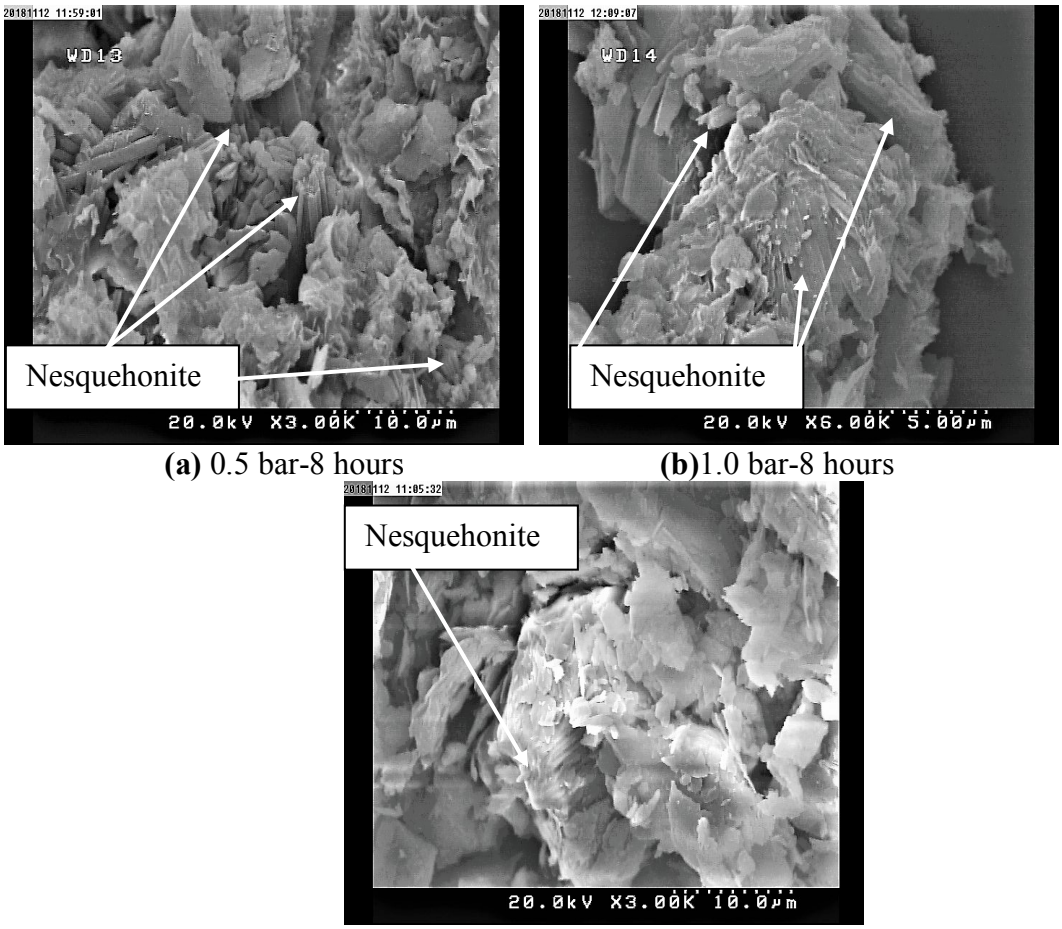
Fig.6. Percentage of mass increment of **(a)** 15% MgO-stabilized soil carbonated under different pressures of CO_2 at different periods.**(b)** Different MgO-stabilized soil carbonated under 1.5 bar pressure of CO_2 at different periods



(a) Natural soil **(b)** MgO-0 day

(c) MgO-7 days **(d)** MgO-14 days

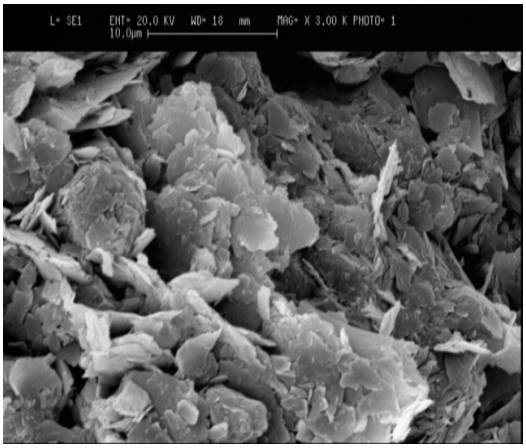
Fig.7. Scanning electron micrograph of natural soil and stabilized soil with 10% MgO at different curing times (a, b, c, d)



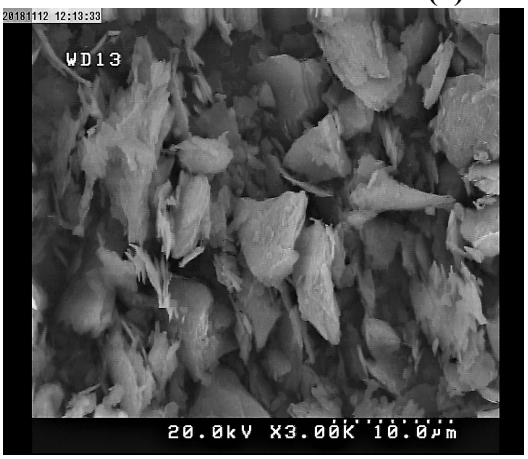
(a) 0.5 bar-8 hours **(b)**1.0 bar-8 hours

(c) 0.5 bar-24 hours

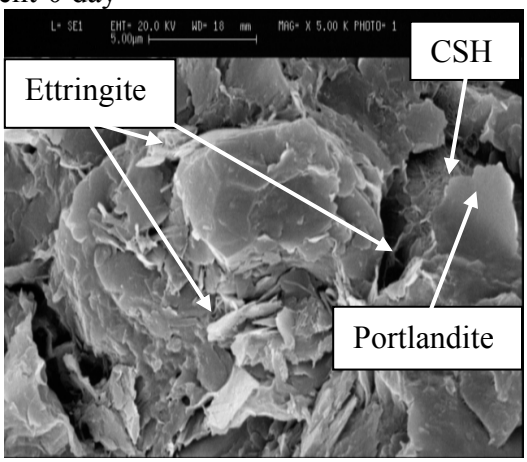
Fig.8. Scanning electron micrograph of stabilized soil with 10% MgO under 0.5 and 1.0 bar at period of 8 hours (**a** and **b**), and 0.5 bar at period of 24 hours (**c**)



(a) Cement-0 day

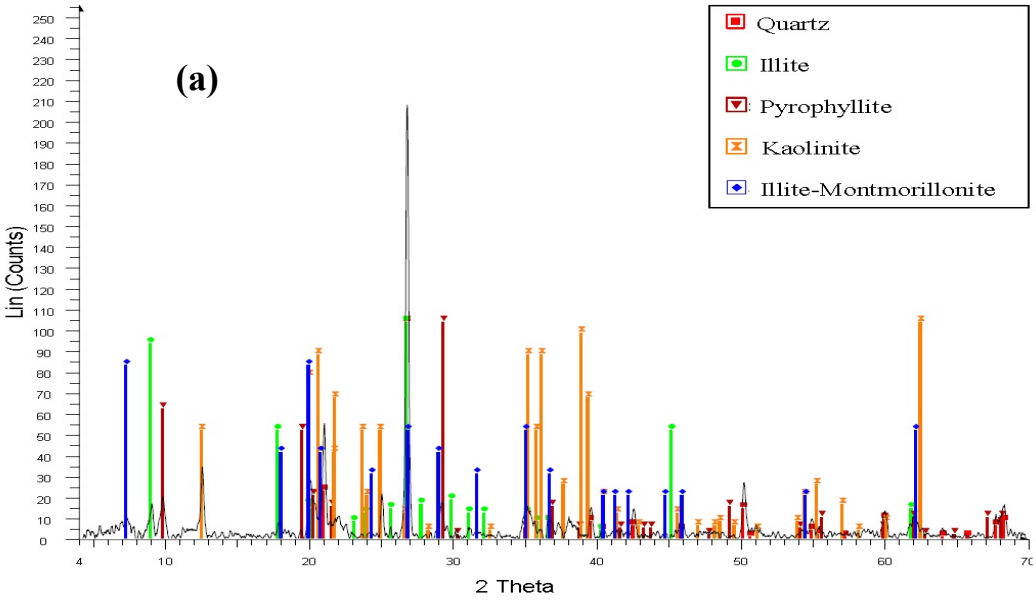


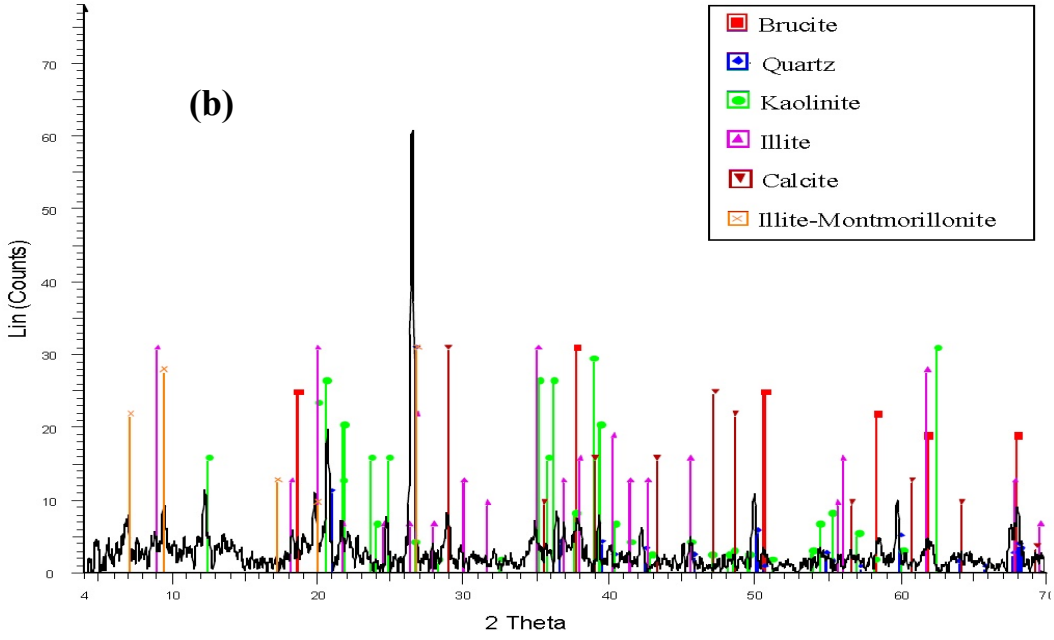
(b) Cement-7 days



(c) Cement-14 days

Fig.9. Scanning electron micrograph of natural soil and stabilized soil with 10% cement at different curing times


(a)
Quartz
Illite
Pyrophyllite
Kaolinite
Illite-Montmorillonite
Lin (Counts)
2 Theta


(b)
Brucite
Quartz
Kaolinite
Illite
Calcite
Illite-Montmorillonite
Lin (Counts)
2 Theta

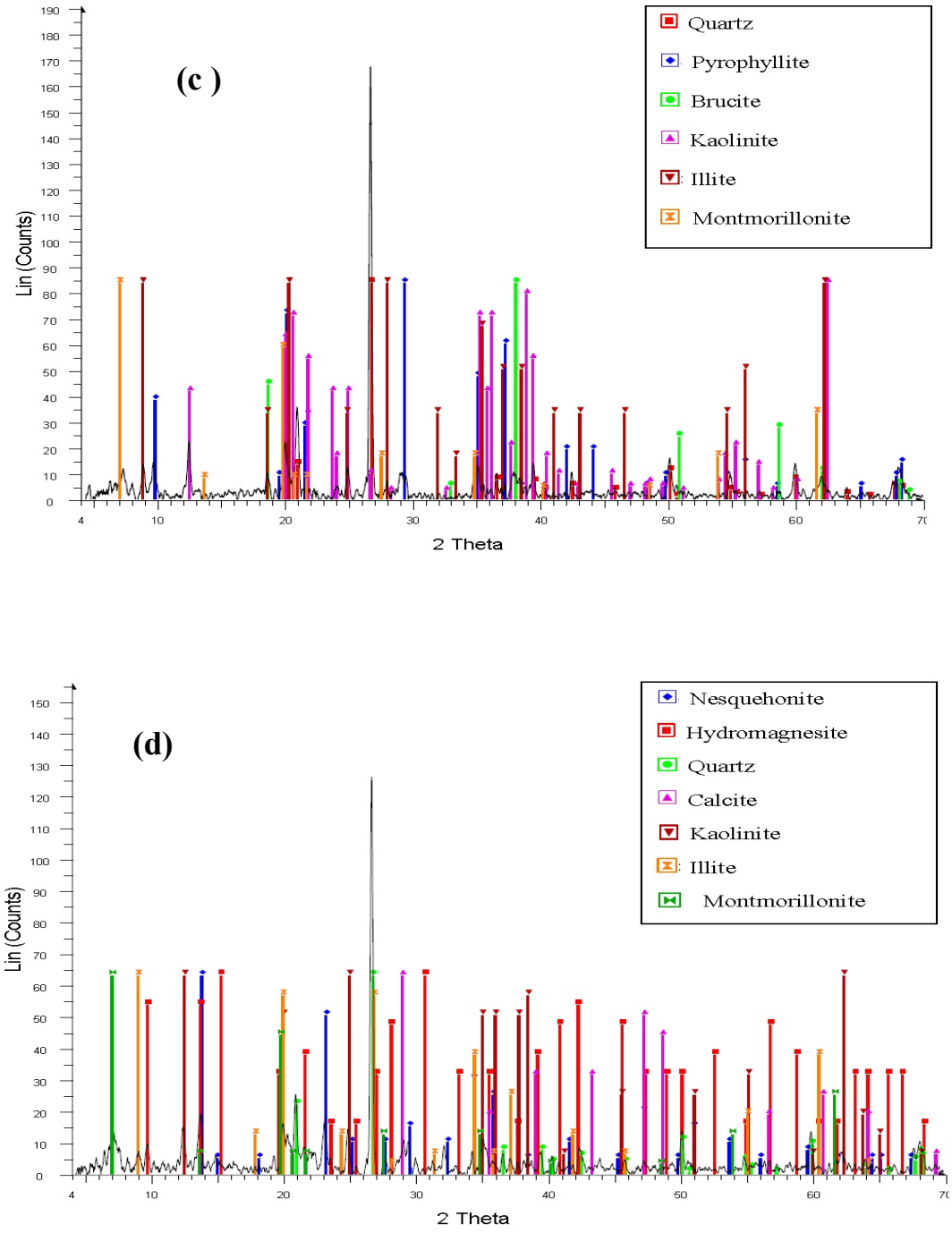


Fig.10. XRD diffractogram for soil stabilized with 10% MgO at different conditions**: (a)** 0 day **(b)** 7 days, **(c)** 14 days. **(d)** Forced CO_2 with 0.5 bar pressure for 24 hours

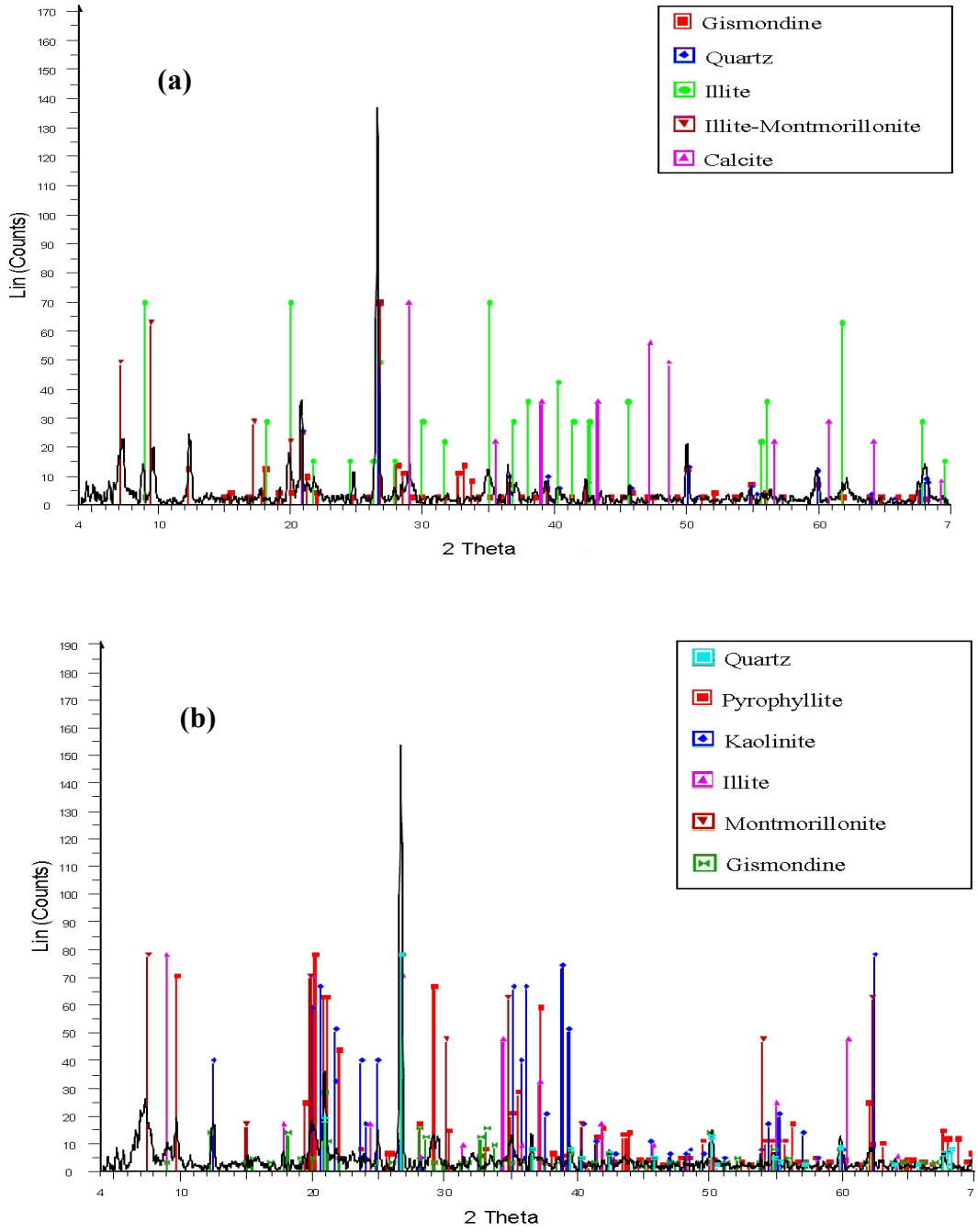


Fig.11. XRD diffractogram for soil stabilized with 10% cement at different conditions**: (a)** 7 days, **(b**) 14 days.

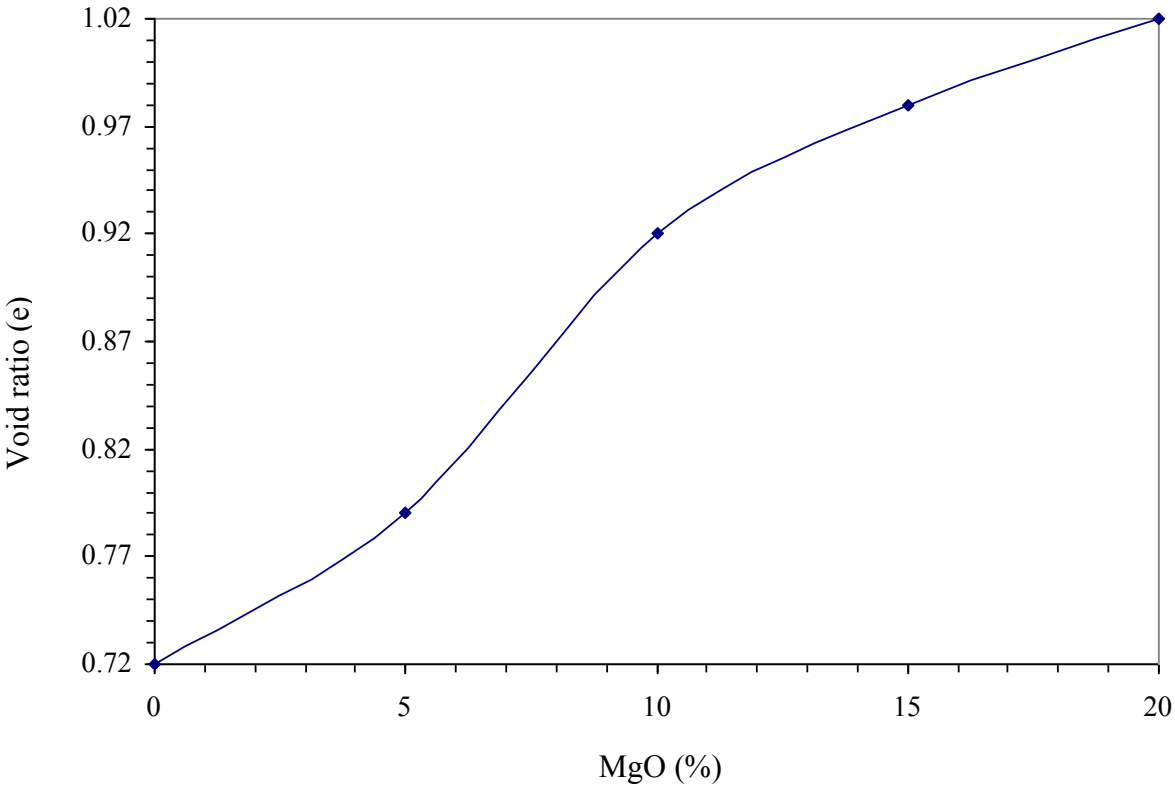


Fig.12. Variations of void ratio against different MgO contents for different mixtures of soil and MgO during standard compaction